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REVIEW

Freshwaters: which NOM matters?

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Abstract One of the difficulties encountered in the study of natural organic matter (NOM) in aquatic environments concerns terminology: a large number of different names and acronyms are used. In fact, this diversity merely reflects the variety of approaches applied to the study of NOM, leading to the definition and measurement of different operationally-defined fractions. As a result, the choice of the 'best' method to use and of the 'best' fraction to work on in a particular case is far from straightforward. This has as a consequence that often very simple methods for NOM characterisation are used in applied environmental studies and surveys. This study includes, first, a review of the most widely applied terminology, as described in over 500 articles, and, second, a first attempt at assessing how the panoply of methods available is really used in applied environmental studies.

Keywords Natural organic matter · NOM · Organic carbon · DOC · TOC · Fulvic · Humic

The list of acronyms given in Tables 1–5 is not exhaustive. This list will be regularly updated at http://www.schema.lu. Readers are kindly requested to send to the author any acronym they find that is not listed in the tables.

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Introduction

The term "natural organic matter" (NOM) is normally used to designate all the organic matter in a reservoir or natural ecosystem other than living organisms and compounds of man-made origin. The NOM found in natural waters possesses a large variety of properties and is composed of an extremely complex mixture of compounds, most of which have not yet been identified. Because of the diversity of the natural processes of synthesis and degradation, the number of constituents in this mixture can be considered to be 'infinite', and therefore there is little hope of completely separating and identifying them. Consequently, studies of NOM have nearly always been concerned not with pure compounds but rather with groups of compounds separated from the initial mixture, or simply observed, by means of different techniques. Since the properties of these compounds vary widely, it is no surprise that this 'blind' approach often yields results that depend on the origin of the sample and/or on the separation procedure used, thereby rendering sample intercomparison, and even understanding of the data, difficult. In spite of these drawbacks, NOM-related measurements are continuously being made in many different fields ranging from basic laboratory studies to management and policy related controls. As a result, the term 'natural organic matter' effectively means rather different things to different organic matter 'users'.

Recent years have witnessed important advances in analytical chemistry, particularly in the fields of chromatography and spectroscopy. These have led to the development of new, increasingly sophisticated methods for characterising isolated fractions of NOM and brought about the publication of a profusion of characterisation-oriented articles, mainly by the 'humic substances'

community. Reviews of these methods are plentiful [see, for instance, Abbt-Braun et al. (2004) and McDonald et al. (2004)]. However, this flourishing academic research has tended to obscure the fact that there is a large gap between theoretical developments and the actual measurements being taken in applied studies.

The first part of this article briefly reviews well-known concepts and ideas, as described in over 500 articles, with the objective of clarifying the confusion surrounding the extensive terminology related to NOM in freshwaters. The second part is an attempt to evaluate the 'reality' in some fields of application through an exhaustive review of all the papers published in two well-known applied journals over a recent period (2001–2005). These journals are not devoted solely to the study of natural organic matter. This choice is intentional: the first objective of the study is not to establish a list of reference methods or to write another review of state-of-the-art techniques, but rather to appraise the methods actually being used in the field by non-experts in NOM, with the final goal of producing a measure of the existing gap between basic and applied research. We hope that this work makes a useful contribution to facilitating communication among NOM-communities and, particularly, to sharing existing data on sound grounds.

A walk through a forest of acronyms

Bulk organic carbon measurements

Over the last century, the most common parameter used to quantify NOM in natural waters has been the measure of total (TOC) and dissolved (DOC) organic carbon. For years, a general rule of thumb, which has luckily fallen out of favour, was that the weight of the total organic matter pool was twice that of the measured organic carbon (OC) (Krogh 1934; Sharp 2002). After inorganic dissolved carbon is eliminated, the quantitative estimation of OC concentrations is almost always made by converting it to CO_2. Rapid and complete DOC to CO_2 conversion requires strong oxidation—the most commonly-used methods are wet-oxidation with persulfate and high temperature catalytic oxidation. CO_2 is nearly exclusively measured today using non-dispersive infrared analysers. Though they focus largely on DOC in seawater, the excellent chapters by Sharp (2002), which retrace the historical development of the existing methods, and by Hedges (2002) on the Sugimura controversy, are strongly recommended.

Types of NOM as a function of origin

Depending on the nature of the aquatic system being studied (e.g., small streams vs. large rivers, rivers vs. lakes, pristine vs. populated areas), NOM can include, in variable proportions:

- Pedogenic organic matter (allochthonous): organic matter produced by the decomposition of higher plants by bacteria and fungi and leached from the soil of the drainage basin by rainwater. It is often accepted that it contains compounds with characteristics similar to those of soil fulvic acids. In peat-rich zones, peat-derived NOM can also be leached into water bodies.
- Aquogenic organic matter (autochthonous): formed in the water mass itself, or in upstream water bodies, essentially from excreta and decomposition of plankton and aquatic bacteria.

Depending on the system, organic compounds resulting from human activity can also be present in significant amounts in surface and groundwaters. Different names and acronyms applied to NOM as a function of its origin can be found in Table 1.

Because of their different origins, the various types of organic matter have appreciably different properties. No existing methods permit the *quantification* of the different types of NOM on the basis of their origin. However, the measurement of bulk parameters (see next section) can help to provide an insight into the sources of the NOM present in a given system. NOM origin has also been studied through the use of molecular 'biomarkers': since many structurally unique compounds are produced only within specific organisms and/or environmental settings, they can be used to trace the remains of these different sources back through space, time and variable degrees of degradation.

Bulk measurements

The measurement of bulk parameters has often been used to *characterise* the type of NOM present in a given system. The most widely used parameters are: elemental ratios (C/N, C/O, C/H, C/S), particulate OC/TOC ratio, isotopic ratios ($^{13}C/^{12}C$, $^{15}N/^{14}N$, etc.), and different spectroscopic parameters related to the degree of NOM aromaticity (UV–visible, fluorescence). As mentioned above, these parameters can furnish indications on the origin of the NOM.

The NOM detected by applying these spectroscopic techniques has sometimes been given specific names such as: CDOM or chromophoric dissolved organic matter (Tietjen et al. 2005); CDOM or coloured dissolved organic matter (Gao and Zepp 1998); FDOM or fluorescent dissolved organic matter (Baker and Spencer 2004). Often results obtained by UV–visible have been used as a measure of the total NOM content in a given system. For instance, UV–visible detection is currently used as on-line detection in techniques such as field flow fractionation

Table 1 Some of the acronyms used in NOM-related studies and their meaning in relation to NOM origin

Acronym	Meaning		Reference[a]
AOM	Aquogenic organic matter	Formed in the water mass itself from plankton and bacteria metabolism and degradation	Buffle (1988)
AOM	Algogenic organic matter	Organic matter formed by metabolic processes of microorganisms like cyanobacteria and green algae	Schmidt et al. (1998)
AROM	Aquogenic refractory organic matter	Non-easily degradable fraction of AOM	Buffle (1988)
AntOM	Anthropogenic organic matter	Organic compounds resulting from human activity	Buffle (1988)
EDOC	Excreted DOC		Hama and Handa (1987)
EOC	Excreted organic carbon		Münster (1993)
EOC	Extracellular organic carbon		Søndergaard and Schierup (1982)
EOM	Extracellular organic matter		Hoyer et al. (1985)
EPS	Exopolymeric substances		Hoagland et al. (1993)
IOM	Intracellular organic matter		Pivokonsky et al. (2006)
PDOC	Phytoplankton extracellular products	Compounds produced by 'excretion', 'exudation' or 'extracellular release' of photosynthetically produced organic carbon	Sundh (1989)
PDOC	Photosynthetically produced dissolved organic carbon		Cole et al. (1984)
POM	Pedogenic organic matter	Originated from leaching of soil organic matter	Buffle (1988)
PROM	Pedogenic refractory organic matter	Non-easily degradable fraction of POM	Buffle (1988)
SedOM	Sediment organic matter	Compounds resulting from accumulation and transformation of AOM, POM and organic debris in sediments	Buffle (1988)
SOM	Soil organic matter	Compounds produced in soil, essentially by decomposition of higher plants	Buffle (1988)
TOM	Peat organic matter	Compounds resulting from degradation less advanced than soil organic matter	Buffle (1988)
TOM	Terrestrial organic matter, terrigenous organic matter	Term usually used in ocean studies; terrestrial (Hedges et al. 1997), terrigenous (Mannino and Harvey 2000)	Hedges et al. (1997); Mannino and Harvey (2000)

[a] References are given only to illustrate the use of the term. They are not necessarily the oldest nor the most representative

(FFF). However, users must be aware that the signal obtained is highly dependent not only on the concentration of the NOM present but also on the type (Weishaar et al. 2003). In consequence, a significant amount of NOM can be missed by following this approach.

All the methods mentioned have also been used not only as bulk measurements but also applied to fractions obtained using the techniques described in "Classifications based on fractionation methods".

Types of NOM: operational classifications

The organisation of information in classes or groups that can be recognised, mapped and interpreted is common to any scientific field. This is also the case in NOM studies. However, no entirely satisfactory classification system has been found so far and several NOM classifications coexist. They are function of the analytical approach applied.

Biochemical classification

From a theoretical perspective, the biochemical classification is the best justified. It distinguishes between three major classical groups: carbohydrates, proteins and lipids. These together account for approximately 20–40% of NOM, depending on the system. The rest constitutes a pool of non-classifiable, less-well characterised organic matter that is resistant to degradation.

The determination of the biochemically well-defined compounds has been the source of a number of names and acronyms (Table 2). Methods for determining carbohydrates and proteins can be applied to unmodified samples to quantify free monosaccharides or amino acids, or after hydrolysis of the compounds. Chromatographic and colorimetric methods are available for both types of compounds. However, these methods are not free of problems. For instance, in the case of carbohydrates, lower results are systematically obtained by

Table 2 Some of the acronyms used in NOM-related studies and their meaning in relation to a NOM biochemical category

Acronym	Meaning	Reference[a]
CSP	Coomassie-stainned proteinaceous particles (Long and Azam 1996)	Carrias et al. (2002)
DCH	Total dissolved carbohydrates	Eberlein et al. (1985)
DCHO	Dissolved carbohydrates	Münster (1993)
DCHO	Total dissolved carbohydrates	Hayakawa (2004)
DFAA	Dissolved free amino acids	Münster (1993); Hanisch et al. (1996)
DFAA	Total dissolved free amino acids	Eberlein et al. (1985)
DFCHO	Dissolved free monosaccharides	Hanisch et al. (1996)
DFCHO	Dissolved free carbohydrates	Münster (1993); Jorgensen and Jensen (1994)
DLCFaAc	Dissolved long chain fatty acids	Münster (1993)
DPCHO	Total dissolved polysaccharides	Hayakawa (2004)
DPROT	Total dissolved proteins	Striquer-Soares and Chevolot (1996)
DSCFaAc	Dissolved short chain fatty acids	Münster (1993)
DTAA	Dissolved total amino acids	Münster (1993)
DTCHO	Dissolved total carbohydrates	Münster (1993)
HCl-CHO	Dilute-HCl (0.09 M) hydrolyzable polysaccharides	Hayakawa (2004)
HR-CHO	HCl-resistant polysaccharides	Hayakawa (2004)
MCHO	Monosaccharides (fraction detected without acid hydrolysis)	Hayakawa (2004)
PAA	Particulate amino acids	
PCHO	Polysaccharides	Hung et al. (2005)
PPROT	Particulate proteins	Striquer-Soares and Chevolot (1996)
SPCHO	Water-soluble particulate carbohydrates	Striquer-Soares and Chevolot (1996)
TCHO	Total carbohydrates	Hung et al. (2005)
TDAA	Total dissolved amino acids	Hanisch et al. (1996)
TDCHO	Total dissolved carbohydrates	Hanisch et al. (1996)
THAA	Total hydrolyzable amino acids	Hedges et al. (1994)
TPCHO	Total particulate carbohydrates	Striquer-Soares and Chevolot (1996)
TPOC	Total particulate organic carbon	Hedges et al. (1994)
URA	Total uronic acids	Hung et al. (2005)

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chromatographic techniques as compared to colorimetric methods. A discussion of problems linked to the colorimetric determination of carbohydrates can be found in Chanudet and Filella (2006), while some problems in protein determination are briefly discussed in Perdue and Ritchie (2003). Values close to the detection limit of the techniques are a common problem in both cases. Lipids have an enormous structural diversity and some have been used as biomarkers.

In recent years, the search for major complexants of trace elements, such as copper, in natural waters has boosted interest in the study of another class of compounds: non-protein thiols (glutathione, phytochelatins and low molecular mass thiols), particularly in estuaries and oceans and, recently, in freshwaters (Hu et al. 2006). Phosphorous-containing compounds, such as monophosphate esters, nucleotides and derivatives, and vitamins have been also measured in natural waters.

Categories based on response to colorimetric reagents

Various classes of organic material have been operationally-defined by the colorimetric methods used for their detection. The best known are TEP (transparent exopolymer particles), particles which are transparent on clear slides and can only be directly observed by staining with Alcian Blue (Passow and Alldredge 1994; Grossart et al. 1997). They consist predominantly of polysaccharides. Other cases are the DYP or DAPI (4′,6-diamidino-2-phenylindole) yellow particles (Mostajir et al. 1995; Carrias et al. 2002) and the CSP or Coomassie-stained proteinaceous particles (Long and Azam 1996; Carrias et al. 2002).

Classifications based on fractionation methods

A very common approach to the study of NOM in natural waters has been to divide it into groups, or fractions, each

of which is made up of compounds possessing operationally similar properties (e.g., size, solubility). However, it is important to keep in mind that, although fractionation-based methods may be useful, they always create fractions that are chemically complex mixtures whose composition is entirely dependent on the method used.

Physically-based classification The basic physical size classification is based on the operational distinction between 'dissolved' and 'particulate' matter in natural waters, separated on the basis of filtration through a 0.45 μm (or 0.22 μm) membrane filter. Although it has been repeatedly pointed out that the distinction between particulate and dissolved is arbitrary and of uncertain value, it is now included in most standard analytical methodologies and widely applied: pre-separation of particulate and dissolved phases is embedded in nearly all environmental NOM-related studies.

Although colloids are defined by IUPAC as "molecules or polymolecular particles dispersed in a medium that have at least in one direction a dimension roughly between 1 nm and 1 μm" (Everett 1972), recent years have seen a shift from colloids being generally ignored in NOM studies, and generally included in the so-called 'dissolved' fraction, to being considered as particles with a maximum size of 0.45 μm (or 0.22 μm, depending on the researcher). This phenomenon is closely linked to the increasingly widespread use of various versions of ultrafiltration techniques. These ultrafiltration methods give fractions of organic matter defined by the size of the filters used in the separation. They have often been used coupled with OC measurements to determine the size distribution of NOM. Since no generally-accepted criteria exists concerning the pore sizes of the filters used, size classes vary widely among the different studies and no exact size limits can be assigned to the different fractions listed in Table 3. In practice, since numerous problems related to contamination and adsorption onto membranes have been found, only results from studies where rigorous cleaning and determination of DOC mass balances are performed can be considered reliable. In spite of these facts, the authors of a critical compilation of cross flow filtration (CFF) data for NOM in freshwaters (Town and Filella 2002) were able to establish some trends using the published values. Nevertheless, the use of normalised working conditions is highly recommended.

There has been an increasing tendency these last years to isolate NOM from natural waters by reverse osmosis (RO). Because large volumes of water are needed to obtain gram quantities of NOM, the RO method is attractive since

Table 3 Some of the acronyms used in NOM-related studies and their meaning in relation to the physical fractionation method applied[a]

Acronym	Meaning	Reference[b]
CDOC	Colloidal and dissolved organic carbon	Lock and Ford (1986)
COC	Colloidal organic carbon	
COM	Colloidal organic matter	
CPOC	Coarse particulate organic carbon (>63 μm)	Hedges et al. (1994)
CPOM	Coarse particulate organic matter (>1 mm for Wallace; >63 μm for Hedges)	Wallace et al. (1982); Hedges et al. (1986, 1994)
DNOM	Dissolved natural organic matter	Steiro et al. (2004)
DOC	Dissolved organic carbon	
DOM	Dissolved organic matter	
DOP	Pico- and nano-detrital organic particles	Carrias et al. (2002)
FPOC	Fine particulate organic carbon (<63 μm)	Hedges et al. (1994)
FPOM	Fine particulate organic matter (<1 mm for Wallace; <63 μm for Hedges)	Wallace et al. (1982); Hedges et al. (1986, 1994)
HMW-DOC	High molecular weight DOC	Engelhaupt and Bianchi (2001)
LMWOC	Low molecular weight organic carbon	Allen (1978)
POC	Particulate organic carbon	
POM	Particulate organic matter	
SPOM	Suspended particulate organic matter	Hedges et al. (1986)
TPOC	Total particulate organic carbon	Hedges et al. (1994)
UDOC	Ultrafiltered dissolved organic carbon	
UDOM	Ultrafiltered dissolved organic matter	Hedges et al. (1994)
UOC	Ultrafiltered organic carbon	Martin et al. (1995)

[a] Only acronyms found in freshwaters studies. A much larger variety exists in seawater studies where CFF techniques have been more widely applied

[b] References are given only to illustrate the use of the term. They are not necessarily the oldest nor the most representative

it is rapid and gives high yields without exposing the sample to harsh conditions. Although it is claimed that RO does not to cause any fractionation of the sample (Serkiz and Perdue 1990), it certainly does, as does any physical method of separation, as evidenced by the fact that not all waters give similar carbon recoveries (e.g., Ma et al. 2001). NOM isolated by RO does not receive any particular name.

Chemically-based classification Chemical fractionation procedures yield fractions which may include mixtures, in varying proportions, of the 'biochemical' compounds mentioned above, plus the refractory component of organic matter that does not fit into any of the biochemical categories. For years, the most widely used fractionation technique has been the separation into fulvic- and humic-type components. Humic materials and humic substances are centuries-old terms used to describe coloured organic matter extracted from soils using alkali. The classical operational definition for humic substances is based on solubility differences in acid and basic media, with humic acids being the fraction of humic substances that is precipitated at pH 1 from a solution in base, and fulvic acids being the fraction soluble in aqueous media at all pH values. Nowadays, the most common isolation procedures used for aqueous samples are based on the use of nonionic, macroporous resins (the "XAD resin method") that isolate functionally distinct chemical fractions by polarity (Leenheer 1981; Thurman and Malcolm 1981). Different procedures, often based on the sequential use of various resins, are described in the literature and give a variable number of operationally-defined NOM fractions. This fact, plus an immoderate tendency of some authors to give arbitrary names to the fractions obtained (Table 4), makes it difficult to compare results and pool together available information. Essentially, two families of methods exist: (1) Isolation methods that follow the Leenheer fractionation procedure (Leenheer 1981), which uses three types of resin adsorbents (non-ionic XAD-8, a strong cation exchange resin, a strong anion-exchange resin) and aqueous HCl and NaOH solutions to produce six fractions (hydrophobic and hydrophilic acids, neutrals and bases). (2) Methods that follow the Thurman and Malcolm (1981) large-scale preparative method, in which XAD-8 resin is used to adsorb humic substances from acidified samples. The aquatic humic substances are then back-eluted with NaOH, and fractionated into aquatic humic acids (insoluble at pH 1) and aquatic fulvic acids (soluble at pH 1). Since the mid-1990s, the use of resins in tandem has become widespread (Aiken et al. 1992; Malcolm and MacCarthy 1992): the effluent of an XAD-8 resin column is passed though a column of XAD-4 resin to collect an additional fraction of DOM, of a higher hydrophilic character.

The International Humic Substance Society (IHSS) has adopted the XAD-8 resin method (Thurman and Malcolm 1981) to isolate humic and fulvic acids from natural waters, so IHSS aquatic humic acids contain only hydrophobic organic acids while the IHSS isolation procedure for HA in soils and peats includes no prefractionation based on hydrophobicity.

It must be mentioned that the resin Amberlite® XAD-8 is no longer produced and a substitute resin (Superlite™ DAX-8) has been developed. Slight variations in the humic substances obtained from the two resins have been identified (Peuravuori et al. 2002). This is a proof of the dependence of any classification on the isolation method used.

Lability-based categories

Two important observations in natural waters (rivers, lakes, oceans) are readily apparent: although most of the NOM produced is rapidly consumed, most of the remaining NOM is resistant to biological utilisation. The small fraction of NOM that escapes rapid consumption contributes to the slowly cycling 'biorefractory' NOM reservoir. The bulk NOM pool represents a broad continuum of biological lability ranging from material that turns over on time scales of minutes to days (labile NOM) to material that turns over on time scales of weeks to days (semilabile) and even to material that survives for decades to millennia (refractory NOM).

In some fields, such as in water treatment, only the easily degradable organic matter, directly associated with possible bacterial growth, is of importance. Biodegradable dissolved organic carbon (BDOC) is often defined as the fraction of the dissolved organic carbon which can be metabolized and assimilated by heterotrophic microflora. The classical BOD (biological oxygen demand) is a well-known measurement of this type of approach but often is not specific and/or sensitive enough for determining BDOC in unpolluted waters. Both the BOD and COD (chemical oxygen demand) tests are a measure of the relative oxygen-depletion effect of a waste contaminant and they have been widely adopted as a measure of the effect of pollution. However, the determination of NOM biodegradability by measuring the consumption of DOC by microorganisms during a given incubation period is sometimes preferred. Methods used include the use of plug-flow biofilm reactors, filtration and reinoculation of the sample with a natural assemblage of bacteria, and inoculation with bacteria fixed onto inorganic particles.

Terminology related to NOM that reflects its lability is gathered in Table 5.

Table 4 Some of the acronyms used in NOM-related studies and their meaning as a function of the chemical fractionation method used

Acronym	Meaning	Reference[a]
ABOM	Aquagenic or autochtonous biopolymers (isolation by addition of 95% ethanol)	Wilkinson et al. (1997)
AHS	Aquatic humic substances	Thurman (1985)
AHS	Hydrophobic acids (isolated according to Leenheer 1981)	Imai et al. (2001)
BaS	Bases (isolated according to Imai et al. 2001)	Imai et al. (2001)
Char	Hydrophilic charged compounds (adsorbed by Amberlite IRA-958)	Fan et al. (2001)
DHM	Dissolved humic matter	Münster (1993)
FA	Fulvic acid (fraction of humic substances that is soluble in water under all pH conditions)	
FA	Hydrophobic acid fraction (sorbed on XAD-8 resin at pH 2 and eluted at pH 13)	Aiken et al. (1992)
HA	Humic acid (fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values)	
HA	Hydrophobic acids (adsorbed by Supelite DAX-8, according to Aiken et al. 1992)	Fan et al. (2001)
HbA	Hydrophobic acid fraction (XAD-8 separation)	McCarthy et al. (1993)
HbN	Hydrophobic neutral fraction (XAD-8 separation)	McCarthy et al. (1993)
HIA	Hydrophilic acids (isolated according to Leenheer and Huffman 1976)	Perdue and Ritchie (2003)
HiA	Hydrophilic acids (isolated according to Leenheer 1981)	Imai et al. (2001)
HIB	Hydrophilic bases (isolated according to Leenheer and Huffman 1976)	Perdue and Ritchie (2003)
HI	Hydrophilic fraction (XAD-8 separation)	McCarthy et al. (1993)
HIN	Hydrophilic neutrals (isolated according to Leenheer and Huffman 1976)	Perdue and Ritchie (2003)
HiN	Hydrophilic neutrals (isolated according to Leenheer 1981)	Imai et al. (2001)
HOA	Hydrophobic acids (isolated according to Leenheer and Huffman 1976)	Perdue and Ritchie (2003)
HOB	Hydrophobic bases (isolated according to Leenheer and Huffman 1976)	Perdue and Ritchie (2003)
HON	Hydrophobic neutrals (isolated according to Leenheer and Huffman 1976)	Perdue and Ritchie (2003)
HoN	Hydrophobic neutrals (isolated according to Leenheer 1981)	Imai et al. (2001)
HPIA	Hydrophilic acid fraction (contained in the XAD-8 resin effluent at pH 2 that sorbs on a XAD-4 resin and is eluted at pH 13)	Aiken et al. (1992)
HPO neutrals	Hydrophobic neutral fraction (extracted from the XAD-8 resin by Soxhlet extraction with acetonitrile and water)	Malcolm and MacCarthy (1992)
Neut	Passed through all resin columns (XAD-8, XAD-4, Amberlite IRA-958)	Fan et al. (2001)
NHS	Non humic substances (fraction not adsorbable on XAD-2 or XAD-8)	Abbt-Braun et al. (2004)
NOM-CH	Carbohydrate-rich fraction (adsorptive behaviour on a cross-linked polyvinyl pyrrolidone, PVP, polymer according to Lowe (1975))	Chen et al. (2002)
NOM-PP	Polyphenolic-rich fraction (adsorptive behaviour on a cross-linked polyvinyl pyrrolidone, PVP, polymer according to Lowe (1975))	Chen et al. (2002)
PHA	Peat humic acid	Feng et al. (2005)
ROM	Refractory organic matter	Buffle (1988)

Table 4 continued

Acronym	Meaning	Reference[a]
ROS	Refractory organic substances	Abbt-Braun et al. (2004)
TA	Transphilic acids (adsorbed by Amberlite XAD-4, according to Aiken et al. 1992)	Fan et al. (2001)
WFA	Water fulvic acid	Buffle (1988)
WHA	Water humic acid	Buffle (1988)
XAD-4 acids	Fraction sorbed on XAD-4 resin (effluent of XAD-8 resin at pH 1.95) and eluted by dilute base	Malcolm and MacCarthy (1992)
YOA	Yellow organic acids	Perdue and Ritchie (2003)

[a] References are given only to illustrate the use of the term. They are not necessarily the oldest nor the most representative

Table 5 Some of the acronyms used in NOM-related studies and their meaning when lability criteria are involved

Acronym	Meaning		Reference[a]
AOC	Assimilable organic carbon	AOC is based on the measurement of biomass growth, either by plate count or by adenosine triphosphate measurement	Hem and Efraimsen (2001)
BDOC	Biodegradable dissolved organic carbon	Fraction of dissolved organic carbon which can be metabolized and assimilated by heterotrophic microflora	Servais et al. (1987)
BOD	Biochemical oxygen demand	Amount of O_2 in water consumed by biochemical oxidation of waste contaminants in a given time (5, 20 days)	http://www.standardmethods.org
BOM	Biodegradable organic matter		Kaplan et al. (1994)
COD	Chemical oxygen demand	Amount of O_2 in water consumed by the chemical oxidation of waste contaminants	http://www.standardmethods.org
LDOC	Labile dissolved organic carbon		Laird and Scavic (1990)
LDOM	Labile dissolved organic matter		
LOCP	Labile organic carbon pool		Münster (1993)
ROCP	Recalcitrant organic carbon pool		Münster (1993)
UDOC	Utilizable dissolved organic carbon		Münster (1993)

[a] References are given only to illustrate the use of the term. They are not necessarily the oldest nor the most representative

Real life

The objective of the second part of this article is to assess how real 'users' actually apply the concepts briefly described in the first part of the article and the state-of-the-art characterisation methods described in the specialised literature. The aim is to gain an insight into the basic criteria (type of ecosystem studied, methodological considerations, questions being addressed, other) that guide users in the 'market' of potential fractions and methods as they make their choice. The strategy used was the exhaustive review of all articles published in two applied-oriented journals which are not specifically devoted to organic matter studies. As explained in the introduction, this choice was intentional since the objective is not to establish a list of the 'best' methods to use but rather to obtain a picture of the methods that end-users actually apply.

Science of the Total Environment

The scope of this journal is multidisciplinary and essentially on applied science. It publishes original research on the environment with an emphasis on changes caused by human activities, including mainly papers in applied environmental chemistry and environmental health sciences. It is addressed to environmental scientists, environmental toxicologists, ecologists, chemical/environmental engineers, environmental health scientists and epidemiologists, risk scientists, environmental science managers and administrators. It began publication in 1972.

According to the Web of Science, 1760 original research papers were published in the period under study (2001–2005). Articles were extracted by using the Quick Search procedure available on the journal's website. This procedure makes it possible to search for terms which appear in article titles, abstracts and keywords. The number of

articles retrieved over the study period by using the terms listed is as follows (total number of articles ever published on a subject in this journal in brackets): 'Organic matter', 127 (409); 'Organic Carbon', 103 (332); 'Dissolved Organic Carbon', 43 (118); 'DOC', 31 (70); 'TOC', 14 (45); 'Humic', 20 (323) and 'Fulvic', 8 (117). Around 30% of the papers ever published on these subjects appeared during the period in question, except for papers obtained with 'humic' and 'fulvic' as the keywords, where the proportion is lower (only 6–7%). Other terms such as 'BOD', 'COD', 'DOM', 'NOM', 'OM' and 'POC' did not retrieve new articles except for five articles for 'BOD' and 'COD'. The comprehensiveness of the results obtained was not checked. Since the focus of the study is on freshwaters (field and laboratory studies of surface freshwaters and/or their sediments, and groundwaters), articles which were not relevant were eliminated by manually screening the titles and, where necessary, reading the paper. By following this procedure, the number of articles initially found was reduced to: 'Organic matter', 40; 'Organic Carbon', 38; 'Dissolved Organic Carbon', 23; 'DOC', 17; 'TOC', 11; 'Humic', 12 and 'Fulvic', 3, resulting in a total of 85 papers (some articles were occasionally simultaneously classified in different classes).

The survey of these papers showed that, in most of the articles describing field studies, the only parameter measured was organic carbon, often after filtration (DOC). The review of the procedure used shows an expected lack of unifying criteria concerning filter pore sizes and procedures applied (here and in the following paragraphs, number of articles are given in brackets): unfiltered samples (7), 0.7 μm pore size filters (5), 0.6 μm pore size filters (1), 0.45 μm pore size filters (12), 0.2 μm pore size filters (2), Whatman GF/C (no size mentioned) (1), Whatman GF/F (no size mentioned) (3), Millipore APF/F (no size mentioned) (1), either no size given or no filtration mentioned but DOC values reported (4), centrifugation (no size cut-off mentioned) (1). Only in one study was the organic colloidal fraction isolated by ultrafiltration. Concerning OC determination, most DOC measurements were performed using the HTCO method (15), but wet-oxidation with persulfate (6) and UV-oxidation (1), both with IR detection, were also used. In one case, a portable apparatus incorporating persulfate oxidation and conductimetric detection was applied. In another, DCO (dichromate method) was determined as a surrogate of OC concentrations, accompanied by a correlation with DOC for a limited number of samples. In one article, the only information provided was that non-dispersive IR was applied while another merely gave the name of a piece of equipment which does not appear to be commercially available, without any details of the method used. In both bed and suspended sediments, OC was the parameter most widely measured, usually with an elemental analyser (11). An HTCO apparatus with a solid sample module was used in one case and chemical oxidation with dichromate was used in two articles. When a distinction between POM and POC was made, POM was determined using a loss on ignition (LOI) procedure (9). Temperature and duration of the LOI determination varied widely among the studies. It is noteworthy that in 25 studies, no detailed explanation was given of the method used for DOC/POC determination. These articles sometimes gave references for the methods used (12) or provided values from previous studies (2), or simply supplied no information at all (8). Considering how dependent results are on the filtration procedure and OC method used (Sharp 2002), the publication of studies not containing this information should be strictly avoided. Finally, NOM is largely used in the discussion without any NOM measurement at all being made in a few cases (3).

Only in some articles (12), were parameters other than OC measured for NOM characterisation in the studied systems. This number is amazingly low—only 14% of the total considered. The methods applied are detailed in Table 6. The choice of the techniques was mostly guided by the aim of determining the origin of the NOM.

NOM was included in two field-related articles where trace element speciation modelling was performed. Neither adequately explained the procedure used. In Devez et al. (2005), a single ligand model was used with a stability constant value for Cu measured by DPASV assuming that it was only complexed by NOM but no information is given on the concentration of NOM used in the calculations, and other characteristics such as NOM pK and site density are omitted. In Karlén et al. (2001), it is wrongly assumed that one of the computer codes used (MINTEQA2) cannot take into account binding by NOM and no details are given on the concentrations and ligands used when another code (WHAM) is applied. It is important to stress that, irrespective of other considerations, the speciation distributions calculated are of doubtful value in both articles, simply because of the lack of key information concerning NOM.

Laboratory studies (16) represent less than 20% of the total number of articles considered. The objectives and types of organic matter used are detailed in Table 7. It is interesting to note that the substances used encompass nearly all possible types of natural organic matter, ranging from humic-type substances to carbohydrates of bacterial and algal origin. This palette is in strong contrast with the approaches used in field studies where the type of NOM present is barely considered.

Journal of Hydrology

This journal publishes research papers and reviews in all the subfields of the hydrological sciences, including

Table 6 Studies published in *Science of the Total Environment* (2001–2005) where parameters other than organic carbon are measured

Parameter measured	Type of system	Reason given for the measurement of the parameter	Reference
IR in the vertically attenuated total reflectance mode (VATR)	River suspended sediments	Identification of organic components	Hillier (2001)
C/N ratio	River suspended sediments	Identification of the NOM origin	Hillier (2001)
	Sediments and zooplankton	Trace the origin of POM	Kainz and Lucotte (2002)
	Freshwater sediments	Identification of the NOM sources	Leite Silva and Rezende (2002)
	Suspended and bed sediments	None	Tareq et al. (2003)
	Urban catchment suspended sediment	Used to trace NOM origin (vascular plants *vs.* plankton)	Bibby and Webster-Brown (2005)
	Ice, snow, ice-rafted debris, ice-interstitial water, seawater	Used to assess POM origin	Gustafsson et al. (2005)
$^{13}C/^{12}C$ ratio	Sediments and zooplankton	Trace the origin of POM	Kainz and Lucotte (2002)
$\delta^{13}C$	Ice, snow, ice-rafted debris, ice-interstitial water, seawater	Used to assess POM origin	Gustafsson et al. (2005)
A_{340}	Filtered (GF/C) river water	"To provide data from this established technique and to provide a check for inner-filtering effects"	Baker and Spencer (2004)
A_{254}/DOC (SUVA)	Impact of rainstorm events at a water treatment works	Description of NOM characteristics	Hurst et al. (2004)
Absorption spectrum, $\lambda = 350$–700 nm	Laboratory study	None, but highest absorbances at lowest λ tentatively related to exudate composition	Lanzillotta et al. (2004)
A_{254}/DOC, A_{254}/A_{400}	Laboratory study	Parameters related to the unsaturation (A_{254}/DOC) and molecular weight (A_{254}/A_{400}) of "humic molecules"	Trulleyová and Rulík (2004)
SUVA (no λ given)	Laboratory study	None	Huang et al. (2005)
Fluorescence excitation–emission matrix (EEM)	Filtered (GF/C) river water	Determination of the source of NOM	Baker and Spencer (2004)
Fluorescence $\lambda_{ex}/\lambda_{em}$: 366/450	Unfiltered river water	"Information relating to the structure and conformation" of "humic substances"; study of NOM-Cu complexation	Patel-Sorrentino et al. (2004)
Scanning electron microscopy (SEM)	Urban catchment suspended sediment	Investigation of particle characteristics	Bibby and Webster-Brown (2005)

physical, chemical, biogeochemical aspects of surface and groundwater hydrology and hydrogeology. Papers have empirical, theoretical and applied orientations. It began publication in 1963.

Over the period under study (2001–2005), 1,313 original research papers appeared in this journal (Web of Science). Articles were extracted using the procedure described above. The same keywords were used. The number of articles found over the study period is as follows (total number of articles ever published for each category in this journal in brackets): 'Organic matter', 18 (67); 'Organic Carbon', 21 (76); 'Dissolved Organic Carbon', 17 (51); 'DOC', 12 (32); 'TOC', 3 (7); 'Humic', 2 (5); 'Fulvic', 2 (10), 'BOD' 2 (5), 'COD' 4 (11), 'DOM' 1 (3), 'NOM' 0 (1), 'OM' 0 (1) and 'POC' 0 (1). The comprehensiveness of the results obtained using these keywords was not checked but a random inspection showed that a certain number of papers containing organic matter measurements had not been identified by using the above keywords. Nevertheless, only papers found by using the standard procedure were taken into account. After eliminating six papers that dealt with organic matter in soils, 34 papers were left.

DOC/TOC measurements in water samples were performed in only 16 papers. As with *Science of the Total Environment*, all types of filter pore sizes were applied: unfiltered samples-TOC determination (2), 0.7 μm pore size filters (2), 0.45 μm pore size filters (3), 0.2 μm pore size filters (3), Whatman GF/C (no size mentioned) (1), Whatman GF/F (no size mentioned) (1), either no size or no filtration mentioned but DOC values reported (4). Concerning OC determination, DOC determinations were

Table 7 Type of organic matter used in laboratory studies published in *Science of the Total Environment* (2001–2005)

Objective of the study	Type of organic matter	Reference
Adsorption of Hg and Cd on goethite	Rådsla fulvic acid	Bäckström et al. (2001)
Inhibition of human plasmin by humic acids	Isolated from drinking wellwater by absorption on XAD-7 column and Sephadex G-25 according to Aiken et al. (1979)	Hseu et al. (2001)
Cu partitioning onto suspended particulate matter	Suwanneee River NOM concentrated by reverse osmosis	Lu and Allen (2001)
Chemical and microbial reduction of ferric ion	• NOM isolated from a wetland pond by using a cross-linked polyvinyl pyrrolidone (PVP) polymer, as described in Lowe (1975) • IHSS soil humic acid	Chen et al. (2003)
Fenton degradation of hydrophobic organics	IHSS Suwannee River humic acid standard	Lindsey et al. (2003)
Establishment of a method for dissolved gaseous Hg determination	Humic substances from a lake dam by the XAD-8 method (Thurman and Malcolm 1981)	O'Driscoll et al. (2003)
Effect of NOM on metal toxicity measured by the Microtox test	IHSS Suwannee River fulvic acid standard	Hsieh et al. (2004)
Impact of rainstorm events at a water treatment works	Aldrich humic acid	Hurst et al. (2004)
Photo-formation of dissolved gaseous mercury	In situ and filtered cell exudates produced by algae (*Chaetoceros* sp.)	Lanzillotta et al. (2004)
Toxicity of OM to *Daphnia magna*	• River NOM extracted by reverse osmosis • IHSS Suwanneee River NOM isolated by XAD • Synthetic HS1500 humic (free from S, N)	Meems et al. (2004)
Permeation liquid membrane (PLM) related Pb toxicity	IHSS river standard fulvic acid	Slaveykova et al. (2004)
Effect of NOM on metal toxicity to amphipods	Nutrient-rich pond NOM extracted by centrifugation + reverse osmosis + cation exchange resin	Timofeyev et al. (2004)
Comparison of BDOC methods	• Filtered (0.4 μm) stream water • Filtered (0.4 μm) 24 h leaching of alder leaves	Trulleyová and Rulík (2004)
Test of laboratory scale tidal flow reed bed system for water treatment	Diluted raw pig slurry	Zhao et al. (2004)
Bioaccumulation of BaP in *Daphnia magna*	• POM of bacterial origin (reactor with VIANDOX + activated sludge) • POM of algal origin (culture of *Selenastrum capricornutum*)	Gourlay et al. (2005)
Determination of disinfection byproducts from ozonation of raw water	OM from a reservoir fractionated according to Leenheer (1981) into humic, fulvic and hydrophilic	Huang et al. (2005)

performed by a HTCO method (7), wet-oxidation with persulfate (4) UV-oxidation (1), TOC-SIN (1). In one case, DOC (*sic*) was determined in unfiltered (!) samples by oxidation with KMO_4, which is in fact a measure of COD. No method was given (TOC values) in one case and just a reference in another. Finally, only inorganic carbon had been determined in one article, natural organic matter was equivalent to tree trunks and vegetal debris in a second one, and only lignins were determined in a third one. Lability-related measurements were performed in some studies: BOD (2), COD (1). COD-UV values were given in one article, but the meaning of the parameter was not clear. POM was determined only in one study through a LOI procedure and OC in sediments was determined in two studies by a HTCO-IR method.

In only three articles was a parameter other than OC used to characterise NOM. In two of them, fluorescence was measured (EEM in Katsuyama and Ohte (2002) and $\lambda_{ex}/\lambda_{em}$: 300/430 in Cruz et al. (2005)) and, in a third one (Wang et al. 2004), FTIR measurements were performed on fractions isolated using the Leenheer (1981) procedure on rainfall, throughfall, stemflow and stream water from

Table 8 Studies published in *Journal of Hydrology* (2001–2005) where models taking into account NOM are described

NOM type	Model NOM compound	Type of system	Model details	Reference
DOC	CH_2O	Leachate attenuation and development of redox zones in a pollution plume downstream of a landfill	Biogeochemical 2D transport code, based in the two-step partial equilibrium approach in coupling the biogeochemical processes	Brun et al. (2002)
DOM	DOM transport described as a non-reactive solute transport	Contaminant transport in riverbank filtration	Kinetic model (1D flow) with two mobile colloidal phases (DOM and bacteria), an aqueous phase (water), and a solid matrix	Kim and Corapcioglu (2002)
BOD	–	River quality	Model based on a cascade of continuously stirred tank reactors (QUASAR)	Sincock et al. (2003)
DOC	CH_2O	Denitrification in a river riparian zone	2D Reactive-transport model	Chen and MacQuarrie (2004)
DOC	–	DOC flux from peat catchments	Combination of empirical equations	Worrall and Burt (2005)
Labile and refractory DOM		Surface water quality	2D Longitudinal/vertical hydrodynamic and water quality model (CE-QUAL-W2)	Ostfeld and Salomons (2005)
NOM	$CH_2O(NH_3)_{0.07}$	Exsolution of N and Ar by methanogenesis in ground water	Hydrogeochemical transport model PHREEQC	Fortuin and Willemsen (2005)

subtropical forests. Only one laboratory study was found; the authors used acetate as a model compound for DOC (Petrunic et al. 2005).

Interestingly, NOM had been included in seven articles where models were described. Measurements had not actually been made in any of these studies, nor did they take account of the fact that different types of NOM simultaneously present in the same waters may have different behaviour (Table 8). In particular, it is worth mentioning that while some of the models dealt with NOM biodegradation and used a substance such as glucose (extremely labile compound) as a surrogate for DOC (not necessarily labile), in another study all NOM was considered to behave conservatively (zero degradation).

What can we learn from this study?

NOM is generally perceived by the 'NOM-lay' scientist and technician as a complex mixture of substances of relatively unpredictable properties. The existence of many acronyms to describe NOM and its fractions reinforces this impression. The extreme variety of methods potentially available to fractionate and/or characterise NOM, together with the difficulty of understanding the pertinence of the information they provide in the context of a specific problem, makes the choice of the 'best' method to use in each particular case difficult at best. As a result, the option most often taken is the simplest one, and bulk NOM is just measured as DOC or TOC and invoked as a 'wild card' in the conclusions when needed. Even if different types of NOM play clearly distinct roles in environmental systems, they are rarely quantified separately, either because the necessary methods are not easily available or because they are unknown to the user. This situation results in a great waste of effort and money. Improved targeting of the type of DOC that is actually playing a role in a particular problem would significantly improve the yield both in scientific and economic terms.

As evidenced by the different approaches applied in field and laboratory studies, a large gap exists between the two communities. While methods available for NOM characterisation seem to be largely ignored in field studies, the reasons underlying the choice of a given type of NOM for laboratory studies do not seem to be based on any need to solve real problems. A great deal of the body of research that has been built up from laboratory studies over the past 15 years represents incremental learning with a poor capacity for transfer to field studies. It is crucial to foster better understanding of the methods available among field 'users' and a more in-depth appraisal of the environmentally-relevant problems among laboratory 'users'.

Lastly, there are two aspects that should not be forgotten. The first is that all methods available, with or without

fractionation, can only give a picture of the underlying 'reality' and that none, alone or combined, will ever be able to fully restore the 'truth'. Although this observation is applicable to any measuring method, and to any system, it is particularly important in the case of the analysis of complex mixtures of compounds that exhibit a strong heterogeneity at any level, as does NOM. It also highlights the importance of understanding the limitations and capabilities of the method applied in each case. The second aspect is the fact that the complexity inherent to NOM represents in itself an important property of these systems and that methods that aim only at reducing it will not necessarily be the best ones to apply. In other words, it is not necessarily true that the properties of these types of systems are the result of the linear addition of the properties of all its components (even if it were possible to identify them). Methods able to account for NOM complexity are sorely needed.

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